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Oxygen Permeation and Stability of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ Membrane According to Trace Elements and Oxygen Partial Pressure in Synthetic Air

Jung Hoon Park[a]*, Jong Pyo Kim[a], Sou Hwan Son[a]

[a]*Greenhous Gas Tesearch Cente, Korea Institute of Energy Research, 71-2, Jang-dong, Yuseong-gu, Daejeon, 305-343, Korea*

Abstract

A dense membrane of perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ has been successfully prepared by polymerized complex method. Oxygen permeation according to carbon dioxide concentrations was measured in the oxygen partial pressure range of 2.1 x 10^{-3} ~0.63 atm and phase stability of membrane were examined using SEM-EDS. The oxygen flux increased with increasing temperature and pressure difference and the maximum oxygen permeation flux through 1.0 mm membrane was ca. 3.7 ml/cm^2·min at 950 ºC. The oxygen permeation in the condition of air and CO_2 (300~700 ppm) in feed stream decreased more than 43% in comparison with air feed stream.

Keywords: $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$; ceramic membrane; oxygen permeation; CO_2 contaminat

1. Introduction

Oxy-fuel combustion is recently focused on one of reduction methods of carbon dioxide from power generation system in view of environmental (climate change) and sustainable (low rank fuel adaptation) point. In addition the oxy-fuel combustion process eliminates nitrogen from the flue gas by combusting a hydrocarbon or carbonaceous fuel in either pure oxygen or mixture of pure oxygen and a CO_2-rich recycled flue gas so that the size of the process can be reduced. However, the cost of production for pure oxygen is so high that oxy-fuel combustion is not commercialized until now. More economical process than existing method is still necessary to commercialize an oxy-fuel combustion system. Recently, membrane system using ceramic mixed oxides has been developed to obtain high efficiency and low oxygen production cost in combustion temperatures above 700ºC. Especially, dense mixed-conducting ceramic membranes such as LSCF type [1-3], LSTF type [4, 5] and BSCF type oxides [6] are of significant interest due to potential application for high-purity oxygen separation from air. Among the oxygen ion transport membranes (ITM), perovskite-type (ABO_3) ceramic membranes exhibit the highest oxygen permeability due to their high ionic and electronic conductivity. However, ceramic membrane can be deactivated for long time

* Corresponding author. Tel.: +82-42-860-3766; fax: +82-42-860-3134.
E-mail address: pjhoon@kier.re.kr.

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operation at high temperature over 700°C when air with carbon dioxide supplies as feed gas. This process is originated from reaction between metal and carbon dioxide and formation of carbonate such as $SrCO_3$.

In this work, powder for ionic transport membrane has been synthesized and the oxygen separation experiment has been conducted to investigate the oxygen permeability and the stability of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF-5582) membrane at various CO_2 concentrations and oxygen partial pressure

2. Experimental

2.1. Sample preparation

All powder has been synthesized using polymerized complex method which can synthesizes a homogeneous and pure powder relatively low sintering temperature. The as-synthesized powders were compressed into disks of 20 mm in diameter and 1.0 ~ 2.0 mm of thickness in a stainless steel mold under a hydraulic load by unilateral press (model 25601 series, Specac Limited, U.K.). The green disk sintered at 1353 K for 5 hr. The sintered disk was polished to smooth the surface and to control the thickness of disk with 600 grit SiC. The phase of the powder and the disk before and after sintering was characterized with an X-ray diffractometer (XRD, Rigaku Co Model D/Max 2200-Ultimaplus, Japan).

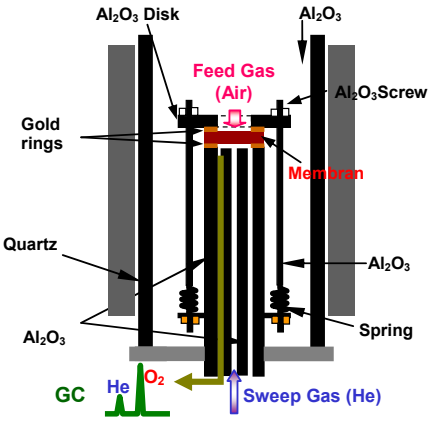


Fig. 1. The schematic diagrams of test cell

2.2. Experimental apparatus and procedure

The membrane permeation cell used in this work is shown in Fig. 1. A disk type permeation cell was used in this work for oxygen permeation study. Au ring (Au plate, 99.9 %, Aldrich) was used as the sealant to seal the disk onto the dense alumina tube. Prior to oxygen permeation test, the cell part is purged with He gas to remove the air in permeation cell tube and to confirm sealing of the assembly consisted of alumina tubes, membrane and sealant for 20 hr. The leakage test for the outer parts of apparatus such as line, fitting and valve was conducted with supplying N_2 gas at feed side. The leakage through membrane during oxygen permeation test was also measured for all runs at each temperature and the oxygen permeation fluxes were corrected on the basis of the measured leakage. Permeation study was performed within the temperature range of 750~950 °C. The temperature of the cell was increased up to 950 °C with a heating rate of 1.5 °C/min and held at desired temperature for 100 min to attain steady state gas flow. Synthetic air (21 vol.% O_2+79 vol.% N_2), Synthetic air with a small amount of CO_2 (300, 500, 700 ppm) and pure He (99.999 %) were introduced into the different side of the membrane disk, which were controlled by the mass flow controller(MKS 247C). The feed flow rate was kept at 20 ml/min, and sweep flow rate was 20 ml/min on the permeated side. The oxygen content in the permeate stream was measured with a gas chromatograph (GC-TCD, Acme 6000, YoungLin, Korea). Helium was used as a reference gas, and a 1.8 m 5A molecular sieve was employed for gas detection.

3. Results and Discussion

3.1. Sample characteristics

Fig. 2 shows XRD patterns of BSCF-5582 according to calcinations temperature. It was confirmed that single-phase perovskite structure was obtained at calcinations temperature over 900 °C. However it was known that the

main crystal structure was carbonate at the temperature less than 900 °C. TGA result also showed the precursor of BSCF-5582 was melted at 1225 °C. Therefore the calcinations condition has marrow temperature windows in the region from 1000 to 1225 °C.

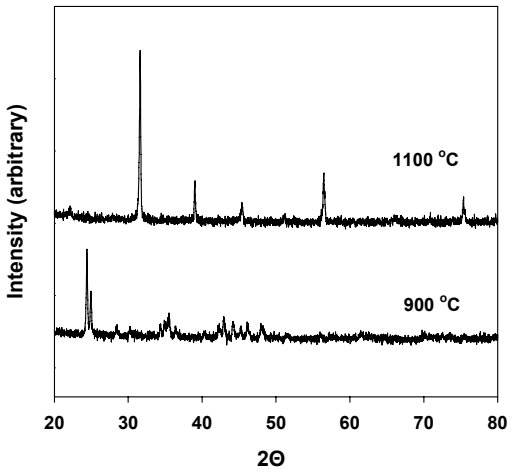


Fig. 2. XRD patterns of BSCF-5582 precursors according to temperature

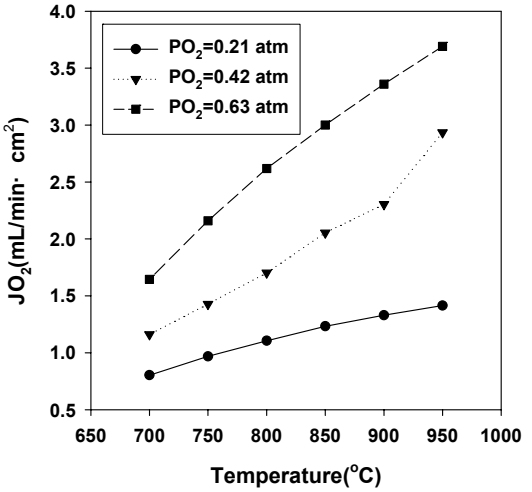


Fig. 3. Oxygen permeation flux of BSCF-5582 membrane according to temperature and oxygen partial pressure

3.2. Oxygen permeation of BSCF-5582 membrane

Fig. 3 shows the oxygen permeation flux for BSCF-5582 membrane. Oxygen permeation flux increased as temperature increased, it reached 1.4 ml/cm^2·min at 950 °C exposed to flowing air (P_h =0.21 atm, feed side of membrane) and helium (P_l =10^{-5} atm, permeated side of membrane). Oxygen permeation flux also increased with

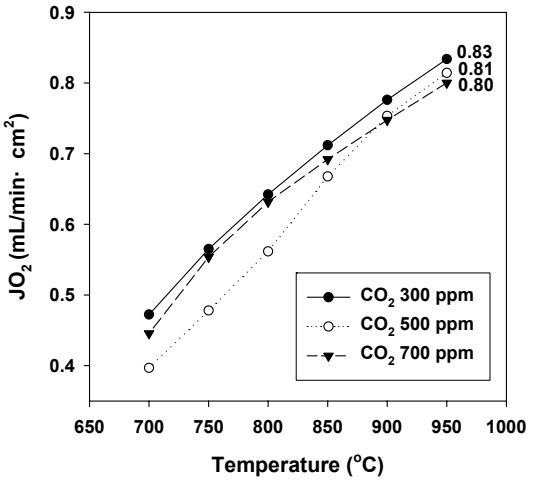


Fig. 4. Oxygen permeation flux at oxygen partial pressure of 0.21 atm

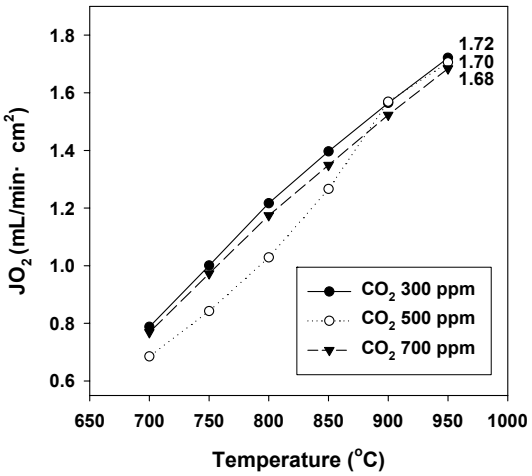
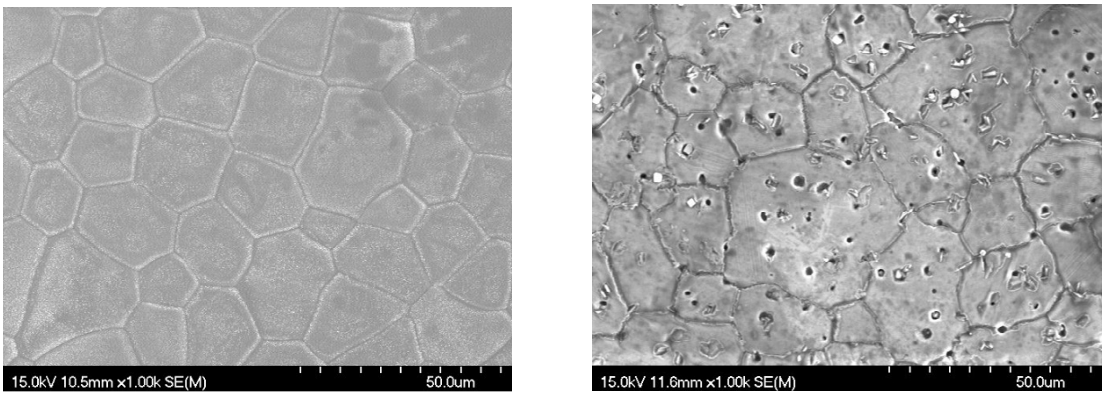


Fig. 5. Oxygen permeation flux at oxygen partial pressure of 0.63 atm

increasing oxygen partial pressure and maximum oxygen permeation flux was ca. 3.7 ml/cm^2·min at 950 ^{o}C with P_h =0.21 atm of oxygen partial pressure according to various temperatures and CO_2 concentrations respectively. In the temperature region below 850 ^{o}C, the oxygen permeation flux decreased in order of 300 > 700 > 500 ppm while at 900 and 950 ^{o}C, the oxygen permeation flux decreased in order of 300 > 500 > 700 ppm. In addition, the difference of permeation flux according to CO_2 concentrations decreased with increasing temperature and the permeation fluxes reached almost to similar values (0.80-0.83 ml/cm^2·min at 950 ^{o}C and 0.21 atm oxygen partial pressure; 1.68-1.72 ml/cm^2·min at 950 ^{o}C and 0.63 atm oxygen partial pressure). This permeation fluxes are much less than that of permeation tests without CO_2. Moreover the value of low permeation flux is maintained after switching CO_2 and air to synthetic zero air. In comparison with Fig. 3, it was known that the oxygen permeation flux decreased much than 43% at atmosphere of CO_2. It indicates that the membrane is deteriorated by carbon dioxide. These results are very important when real air is used as feed gas to separate oxygen because real air has about 300 ppm carbon dioxide.

3.3. Membrane stability

Fig. 6 shows the SEM images of membrane before and after permeation with CO_2 impurity. These images show the surface of permeation side in BSCF-5582 membrane. Before permeation, the surface of membrane looks like dense and clean and grain boundary is shown in this figure but the surface of membrane is deteriorated and gas some holes. It is not clear why the hole occur on the surface. Though it is no problem during permeation test for 100 hrs, this hole formation can make the pin hole (open porosity) for long operation.



(a) (b)

Fig. 6. SEM images of BSCF-5582 membrane before and after permeation with CO_2 impurity; (a) before permeation (b) after permeation

Fig. 7 shows EDS mapping images for feed side surface of BSCF-5582 membrane after permeation test. The surface of feed side was not polished because the roughness of surface in feed side could increase the permeation flux. From Fig. 7, it was known that carbon existed on the surface of membrane after permeation test. It indicated that decrease of permeation flux might be originated from the formation of carbonate. Unfortunately, strontium or/and barium of BSCF-5582 membrane is ease to convert into carbonates such as $BaCO_3$ or $SrCO_3$ when these metals contact with CO_2. Therefore the pretreatment system for removing CO_2 from feed stream may be needed to apply BSCF-5582 as ITM membrane when the real air is feed gas for oxygen separation.

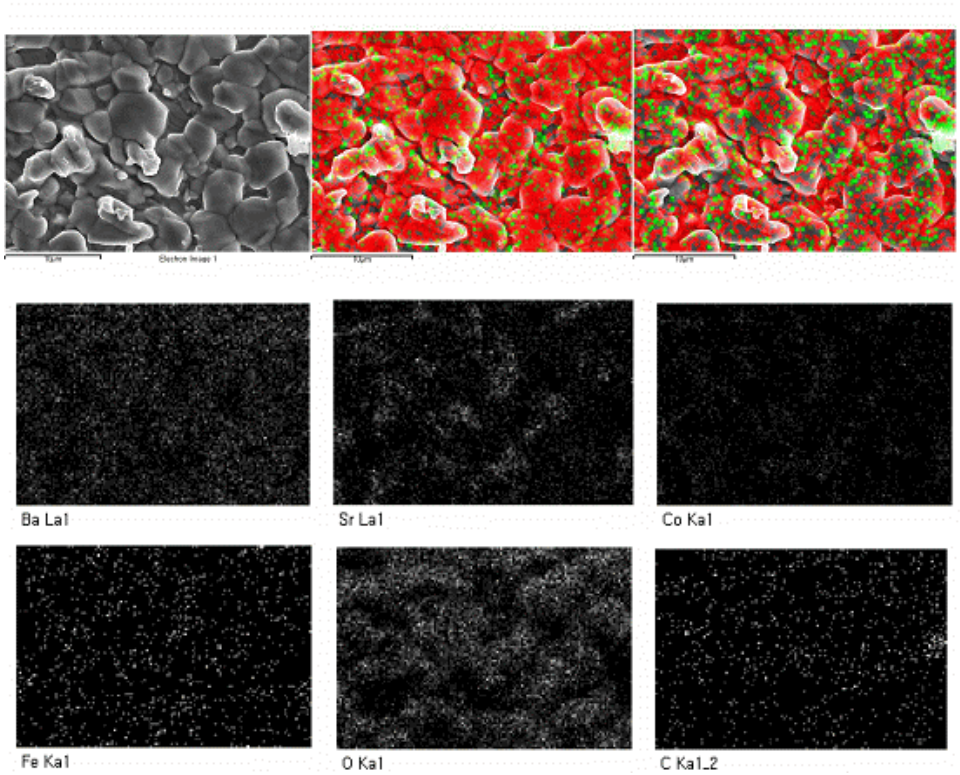


Fig. 7. EDS mapping images for feed side surface of BSCF-5582 membrane after permeation test

4. Conclusion

Perovskite type ceramic oxides $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF-5582) was synthesized by polymerized complex method. The characterization results showed that the oxides prepared possessed perovskite structure without secondary phase in narrow sintering temperature region between 1000 and 1100 ^{o}C. the oxygen flux of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane increased with increasing temperature and oxygen partial pressure, and the oxygen permeation flux through 1.0 mm membrane exposed to flowing air (P_h =0.21 atm) and helium (P_l =10^{-5} atm) was ca. 1.4 ml/cm^2·min at 950 ^{o}C. As the oxygen partial pressure increased from 0.21 atm to 0.63 atm, the oxygen permeation flux increased and reached ca. 3.7 ml/cm^2·min at 950 ^{o}C. In comparison of oxygen permeations as to CO_2 concentration, it was known that oxygen permeation flux with synthetic air and CO_2 as feed gas decreased below 43% than that with only air feed gas. Low oxygen permeation flux of BSCF-5582 membrane might be originated from carbonate formation due to the reaction between Ba and/of Sr metal and carbon dioxide.

Acknowledgment

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